

THE ESTIMATION OF SMALL AMOUNTS OF BARIUM AND STRONTIUM IN SILICATE ANALYSIS.¹

BY W. F. HILLEBRAND.

IN testing qualitatively for barium and strontium in the course of analysis of natural silicates it has probably been the custom to rely upon the spectroscopic examination of the ignited calcium oxalate, on the assumption that, notwithstanding the well-known greater solubility of barium and strontium oxalates over the corresponding calcium salt, the latter would carry down enough of the former to render detection of barium and strontium by aid of the spectroscope a matter of no difficulty.

This assumption in the case of strontium is well founded as I have observed times without number, but it may be entirely fallacious in the case of barium. The twice precipitated calcium oxalate of the analyses marked "later" in the next following paper, afforded a very strong spectroscopic reaction for strontium, but failed to give one for barium, although the oxide of this element was a constituent of the rocks up to 0.76 per cent., and simply because the latter had been entirely kept in solution by the large amounts of ammonium chloride present. This observation suggested at once an explanation for the apparent rarity of barium in the silicate rocks of the earth's crust, and opened up a field for investigation as to the best course to pursue in the separation and estimation of the three alkaline earth metals under the conditions generally prevailing in rock analysis, that is to say, great excess of calcium over barium and strontium in presence of magnesium and large amounts of sodium and ammonium chlorides.

Brief consideration sufficed to reject recourse to collective precipitation of the alkaline earths by ammonium carbonate because of the well-known incompleteness of such precipitation under the prescribed conditions.

It seemed better to seek a separation of barium at the outset. This conclusion was fortified by the results of experiments undertaken to ascertain the behavior of strontium under conditions similar to and differing from the above. A large number of experiments were made with calcium, strontium, and barium sepa-

¹ Read at the Baltimore meeting, December 27, 1893.

rately, and then with mixtures of the former and either strontium or barium. The absolute amounts experimented with were kept low in order that the conditions usually obtaining in rock analysis might be as nearly as possible preserved. It was not for a moment expected that an exact method of separating considerable amounts of barium from either calcium or strontium would be discovered. The most that was hoped for was to work out a method suitable of application where relatively small amounts of strontium and barium occur with relatively large amounts of calcium. The outcome only in a measure fulfilled the hope raised by a few preliminary tests, but the results seem to be of sufficient interest to merit somewhat detailed description.

The precipitates were formed in ammoniacal solution at a boiling heat and were allowed to stand over night before filtering. They were washed but once or twice with cold water because of the very marked solubility of both strontium and barium oxalate in hot water, and even in cold water if the washing is prolonged. The filtrates were evaporated to dryness, ammoniacal salts were removed by heat, and after solution of the residue strontium and barium were precipitated as sulphates, the former after addition of alcohol. The sulphates were, when necessary, tested spectroscopically. The amounts of the different salts taken are purely arbitrary, except that the highest weights for BaO are the chemical equivalents of the highest for SrO.

FIRST SERIES.

	Amount taken calculated as oxide.		(NH ₄) ₂ C ₂ O ₄ · H ₂ O amount in excess of that required for conversion of total bases to oxalates.	NH ₄ Cl Grams.	Total bulk of solution. Cubic centimeters.	SrO in filtrate.	
	SrO	CaO				Weight.	Per cent.
1	0.0343		1	10	250	0.0080	23.3
2	0.0343		1	10	250	0.0045	13.1
3	0.0343		2	10	250	0.0032	9.3
4	0.0343	0.0560	1	10	250	0.0036	10.5
5	0.0343	0.0560	2	10	250	0.00275	8.0
6	0.0343	0.0560	2	10	250	0.0023	6.7
7	0.00384	0.0560	1	5	250	0.0003	7.8
8	0.00384	0.0560	1	10	250	0.0005	13.0
9	0.0010	0.0560	1	5	250	Faint spectroscopic trace.	
10	0.0010	0.0560	1	10	250	" " " " " " " "	

From the above it is plain (1-3) that, as was to be expected, strontium is incompletely precipitated by ammonium oxalate in slight excess and that its solubility is markedly lessened by increase of the precipitant. Furthermore (4-6), that calcium if present in quantity exercises a notable effect in promoting completeness of precipitation. Finally, that with very small amounts of strontium and a great excess of calcium the precipitation of the former is practically perfect in presence of a sufficient excess of ammonium oxalate, irrespective of considerable variations in the ammonium chloride. Additional experiments in which 5-6 grams of sodium chloride were added showed that this salt exercised a very slight but appreciable solvent effect on strontium oxalate. In entire absence of ammonium chloride on the other hand, precipitation of as much as 0.004 gram SrO is practically perfect in presence of 0.0560 CaO.

SECOND SERIES.

	Amount taken calculated as oxide.		(NH ₄) ₂ C ₂ O ₄ ·H ₂ O, amount in excess of that required for conversion of total bases to oxalates. Grams.	NH ₄ Cl Grams.	Total bulk of solution. Cubic centimeters.	BaO in filtrate.	
	BaO	CaO				Weight.	Percentage.
11	0.0599		1	5	250	0.0230	45.2
12	0.0599		1	5	250	0.0089	17.5
13	0.0599		2	5	250	0.0070	13.7
14	0.0599		4	5	250	0.0051	10.0
15	0.0599		1	10	250	0.0457	89.8
16	0.0599		1	10	250	0.0243	47.7
17	0.0599		2	10	250	0.0138	27.1
18	0.0599	0.0560	1	5	250	0.0436	85.6
19	0.0599	0.0560	1	5	250	0.0293	57.5
20	0.0599	0.0560	1	10	250	0.0489	96.0
21	0.0599	0.0560	1	10	250	0.0458	90.0
22	0.0599	0.0560	1	10	250	0.0463	90.9
23	0.0599	0.0560	1	10	250	0.0346	68.0
24	0.0599	0.0560	1	10	250	0.0206	40.5
25	0.0135	0.0560	1	5	250	0.0109	80.7
26	0.0135	0.0560	1	10	250	0.0106	78.5
27	0.00906	0.0560	1	5	250	0.0074	81.7
28	0.00906	0.0560	1	10	250	0.0079	87.2
29	0.00226	0.0560	1	5	250	0.00177	78.3
30	0.00226	0.0560	1	10	250	0.00197	87.2

In this series (11-17) the same action of precipitant and ammonium chloride that was observed in the first series makes itself manifest, only in much greater degree. Numbers 18-24 show in general the marked effect of small variations in the

amount of precipitant, although an exception may be noted in 22 when compared with 21. Comparison of 19 and 22 with 11 and 15 respectively shows that the presence of calcium exerts no retentive effect whatever on the barium, in marked contrast with its behavior toward strontium. With decreasing amounts of barium, the calcium remaining constant as well as the excess of precipitant, the slight influence of large variations in the ammonium chloride is apparent from numbers 25-30. The general result is to show conclusively that considerable amounts of barium may be separated almost completely from calcium by a single precipitation with ammonium oxalate in presence of considerable ammonium chloride, provided the precipitant is used in slight excess only.¹ Additional tests have shown that sodium chloride, as with strontium, slightly facilitates the separation from calcium; also that a double precipitation will effect the quantitative separation of over two mgms. BaO from fifty-six mgms. CaO under the conditions of experiments 29 and 30. In cases like the last the whole of the BaO has been recovered from the filtrates and from the calcium as nitrate no trace of barium could be separated by ether-alcohol. It goes without saying that by increasing the ammonium chloride still larger amounts of barium may be equally well separated, as has been proven by numerous tests.

In endeavoring to apply the knowledge thus gained to the separation of barium from both calcium and strontium, which is the problem usually encountered in silicate rock analysis, difficulties at once suggest themselves, namely, those arising from the partial solubility of strontium oxalate in ammonium chloride, from the presence of five to ten grams of fixed alkali salts, whereby the exact recovery of barium and the strontium that may have gone into solution with it is rendered much less certain, and furthermore, from the increased solubility of the oxalates of the calcium group when, as is very often the case, magnesium is present in some quantity.

Of several experiments made to test the degree of accuracy attainable, first in absence of sodium chloride, then in presence

¹ This fact was first observed by the writer in 1884, and was mentioned in a foot note to p. 592, appendix B., of Mr. S. F. Emmons's *Monograph on the Geology and Mining Industry of Leadville*.

of that salt and also of one of magnesium, thus reproducing the unfavorable conditions usually encountered in actual practice, the following will serve as fair examples.

1. CaO , 0.0560; BaO , 0.0023; SrO , 0.00095; $(\text{NH}_4)_2\text{C}_2\text{O}_4$, H_2O , one gram in excess, NH_4Cl , ten grains, total bulk of solution 250 cc. Two precipitations under precisely similar conditions. Found in filtrates, 0.00236 BaO , showing but the merest trace of strontium. Recovered from the, lime, 0.00085 SrO holding fugitive spectroscopic traces of calcium and barium.

2. Precisely as in 1, with addition of $5\frac{1}{2}$ grains NaCl . In filtrates 0.0023 BaO , in lime 0.0006 SrO .

3. As in 2 with addition of 0.09 MgO . In filtrate 0.0023 BaO , in lime 0.0006 SrO .

It is apparent that the results are very satisfactory in 1, but that in 2 and 3 over thirty per cent. of the SrO has escaped detection although all the BaO was recovered. The amounts of both BaO and SrO taken in these tests exceed what is met with in the great majority of igneous eruptive rocks, and the error in SrO may therefore in most cases be disregarded, for after all an absolute error of twenty-five or even fifty per cent. in the estimation of a substance constituting only 0.1 per cent. of a rock is ordinarily of small moment compared with the ability to certify to its presence with approximate correctness.

The procedure for the separation of the alkaline earth metals in silicate rocks as followed by myself with a fair degree of success for some time past, I will now outline, expressly promising, however, that it is not suitable for universal application, but that it seems to be the only one to meet the requirements of ordinary silicate analysis with anything approaching accuracy.

After a double precipitation, which should be made in any case, the ignited oxalate precipitate will contain nearly all the strontia and none of the baryta if the latter does not exceed 0.2–0.3 per cent. of the rock. If a larger quantity than 0.3 per cent. is present the precipitation by ammonium oxalate must be repeated or the rest of the barium subsequently separated from the strontium by ammonium chromate. The strontium is separated from the calcium by extracting the thoroughly dry nitrates (150–160° C.) by ether-alcohol, which as clearly shown by the

recent exhaustive researches of Fresenius¹ is the only one of the older methods at all capable of yielding a fairly satisfactory result. Hereby of course, any barium that might have been retained is also removed. The strontium weighed as sulphate should always be tested spectroscopically for barium, the barium sulphate likewise for strontium, either salt being brought into condition for making the test by reducing for a very few moments the whole or a part of the precipitate on a platinum wire in the luminous tip of the Bunsen burner, and then moistening with hydrochloric acid. If a trace of barium should be found with the strontium the error is insignificant and may be balanced by the strontium remaining with the calcium nitrate.

Before destroying ammoniacal salts, either by ignition or by nitric acid, prior to estimation of magnesia, a few drops of sulphuric acid should be added to precipitate the barium² which otherwise might contaminate the magnesium pyrophosphate. I say *might*, for small amounts of barium, up to 3 or 4 mgms. of oxide, will pass into the filtrate from the ammonio-magnesium phosphate. Only in exceptional cases have I ever found a trace of barium in the pyrophosphate after accidentally or purposely neglecting to effect a prior separation by sulphuric acid.

As to the barium itself it is improper to accept the amount thus separated from the magnesia as representing the total amount in the rock or mineral. It will almost always be found lower than the truth, probably for the reason that there are so many opportunities during the analysis for slight losses in the form of sulphate. Barium is best estimated in a separate portion which may also serve with advantage for the determination of titanium. The powder is decomposed in a capacious crucible with hydrofluoric and sulphuric acids, evaporation being repeated twice at least to ensure removal of all quartz. After volatilization of the excess of sulphuric acid the dry residue is digested with water containing several cubic centimeters of sulphuric acid to surely retain all titanium in solution, and a

¹ *Ztschr. anal. Chem.*, 29, 30, 32, 1890, 1891, 1893. Separation by amyl alcohol as recommended by P. E. Browning, *Am. J. Sci.*, 43, 50, and 314, 1892, has not been tried.

² The barium sulphate thus formed is not separated by filtration till after destruction of the ammoniacal salts, and, if this has been effected by nitric acid, not until after evaporation to dryness.

few drops of hydrochloric acid, and the solution is allowed to settle for some hours. The ignited insoluble matter is evaporated with relatively much sulphuric and a little hydrofluoric acid till the latter is removed and a clear solution results, which is then poured into a few cubic centimeters of cold water. The precipitate will now be free from calcium in all probability, but may contain a little strontium from traces of which it is easily freed by repeating once or twice the solution in strong acid and reprecipitation by water.¹ Unchanged weight after the final precipitation is evidence of purity of the barium sulphate, and the spectroscope should confirm this. These last mentioned manipulations require little expenditure of time even when they have to be repeated, and the result is usually eminently satisfactory. If the first weight of the barium sulphate is but one or two mgms. it is rarely necessary to purify the salt further.

Such is the procedure when only small amounts of barium and strontium have to be estimated. Should they be present in amount exceeding, say, two mgms. for SrO, and four mgms. for BaO, or should with smaller contents a high degree of accuracy be desired, the already difficult analysis presents still greater difficulties. In such cases there remains no other way than to combine the barium and strontium found in the filtrates from the calcium oxalate with the strontium and barium separated from the oxalate itself, and to apply to the mixture the ammonium chromate method of separation as prescribed by Fresenius (*l. c.*). The practiced eye readily learns to judge by spectroscopic test of the ignited and weighed calcium oxide whether strontium is in sufficient quantity to necessitate this course, and the separate determination of barium as above described will decide with regard to that metal.

¹ If the rock happens to contain zircon this may, and probably will, remain with the barium sulphate until removed by appropriate means.